An Approach to Imprint Irganox 1076: Potential Application to the Specific Migration Test in Olive Oil

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ABSTRACT: Irganox 1076 is a hindered phenolic antioxidant commonly added to polyolefins, whose migration from the plastic packaging into the food is regulated by European legislation. The work herein reports on an initial approach to obtain a molecularly imprinted polymer (MIP) for Irganox 1076, a previously nonimprinted target. In a subsequent step, the application of the molecularly imprinted solid-phase extraction (MISPE) to the fatty simulant olive oil is tested to get its determination free of interferences using high-performance liquid chromatography with PDA detector. The influence of five variables, namely porogen, functional monomer, crosslinker, initiator, and initiation method was investigated through the synthesis of miniMIPs. The best results were obtained using methacrylic acid and ethylene glycol dimethacrylate in tetrahydrofuran under UV radiation with 2,2′-azobis-(2-methylpropionitrile). The application of MISPE to olive oil showed the potential of the imprinted polymer to clean up complex matrices. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2866–2874, 2011

Key words: antioxidants; Irganox 1076; food packaging; high-performance liquid chromatography (HPLC); molecular imprinting

INTRODUCTION

In recent years, molecularly imprinted polymers (MIPs) have shown its ability for the solid-phase extraction and cleanup of such complex matrices as biological,[1] environmental samples[2,3] or food,[4–7] for what highly selective extraction techniques are necessary.

MIPs are synthetic polymers with recognition sites able to specifically rebind a target molecule (template). In general, they are obtained by mixing the template with the complimentary functional monomers and crosslinkers in a suitable solvent. After the polymerization, the template can be extracted from the synthesized polymer.[8,9]

Irganox 1076 (Table I) is a hindered phenolic antioxidant commonly added to polyolefins to improve their stability against the effects of thermo-oxidative and photo-oxidative degradation. Their migration from the packaging into the food is regulated by European legislation[10] that establishes a specific migration limit (SML) of 6 mg kg^{-1}. In principle the migration test should be carried out in the own food but to simplify the analysis, aqueous or fatty food simulants can be used.[11] Until the moment there is not any official analytical methodology to determine the migration of this compound in the allowed simulants.

In aqueous food simulants, two analytical methodologies have been developed in our laboratory using liquid–liquid extraction,[12] or solid-phase extraction[13] and high-performance liquid chromatography with UV detector (HPLC-UV), that achieve detection limits quite lower than SML. Dispersive liquid–liquid microextraction followed by HPLC-UV has been also recently proposed for its determination in water at microliter levels.[14] However, its determination in olive oil, the fatty simulant established by the legislation, has shown to be rather more difficult because of the high complexity of this matrix. O'Brien et al.[15] reported the analysis of Irganox 1076 in olive oil using HPLC and a fluorescence detector after the dilution of the sample with acetone, methodology that has been later applied by other authors.[16]

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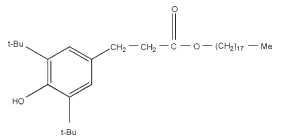
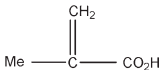
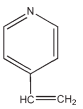
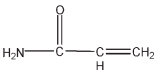
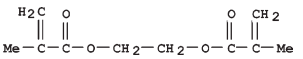
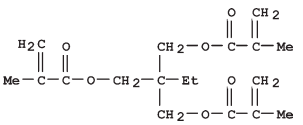
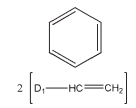
TABLE I
Structures and CAS Numbers of Template, Monomers, and Crosslinkers

Compound	[SciFinder]	CAS	Mw [SciFinder]
Irganox 1076		2082-79-3	530.86
Monomers			
Methacrylic acid		79-41-4	86.09
4-vinylpyridine		100-43-6	105.14
Acrylamide		79-06-1	71.08
Crosslinkers			
EDMA		97-90-5	198.22
TRIM		3290-92-4	338.40
DVB80		1321-74-0	Incompletely defined substance

Different tests performed in our laboratory at SML levels using the more common UV detector instead of fluorescence detector were not successful because of the interferences caused by the olive oil. In these assays either dilution of the sample with an organic solvent or a preconcentration step by liquid–liquid extraction or solid-phase extraction before the chromatographic analysis were tested.[17]

So, this study herein explores the possibility of obtaining an imprinted polymer of Irganox 1076 than can be later used for sample cleanup and/or preconcentration with MISPE. As far as we know Irganox 1076 has not been a target for imprinting, so that no bibliographic data were available. Considering that Irganox 1076 is a phenolic compound with a carboxylate group, the noncovalent imprinting protocol proposed by Sellergren and Andersson[18] was followed.

Many parameters fixed in the polymerization can influence the performance and recognition capacity of MIP for a target template, such as the functional monomer, crosslinker, the porogenic solvent, the initiation method (i.e., thermal or UV initiation), polymerization time, or degasification time. To screen a higher number of variables minimizing the experimental work required, the synthesis of miniMIPs proposed by Sellergren and Andersson[18] and Takeuchi et al.[19] was selected, that consists in the preparation of a quite large number of polymers in small scale.

This work deals with the initial development of a MIP for Irganox 1076 screening polymerization conditions in small-scale followed by the large-scale preparation of the selected MIPs. The application of the imprinted material is subsequently tested in olive oil to determine Irganox 1076 free of interferences using HPLC-UV.

EXPERIMENTAL

Chemicals and apparatus

Methanol and tetrahydrofuran (THF) of HPLC gradient grade were supplied by Merck (Darmstadt, Germany). Dichloromethane of ultragradient HPLC grade was supplied by J.T. Baker (Deventer, The

Netherlands). Water was purified on a Milli-Q Ultrapure system (Millipore, Bedford, MA). Filters 0.2 μm and 13 mm PTFE were from Waters (Milford, MA).

Irganox 1076 was obtained from Ciba (Basel, Switzerland). Acrylamide (>99%), methacrylic acid (MAA, >98%), 2,2′-azobis-(2-methylpropionitrile) (AIBN, CAS 78-67-1, >98%), and ethylene glycol dimethacrylate (EDMA, >97%) were from Fluka, Sigma-Aldrich (Steinheim, Germany); 2, 2-dimethoxy-2-phenylacetophenone (CAS 24650-42-8, 99%), divinylbenzene (DVB80, 80% mixture of isomers), trimethylolpropane trimethacrylate (TRIM), and 4-vinylpyridine (>95%) were from Aldrich (St. Louis, USA). Structures and CAS numbers of monomers and crosslinkers are shown in Table I.

Two different systems with UV lamp were used in the photo-polymerizations: a high-pressure mercury vapor lamp (Phillips, HPK 350 W) and a second system built in the own laboratory. This last one consisted in a reactor equipped with two UV lamps (15 W each, 350 nm), placed in parallel on both sides of the reactor to irradiate the samples in a more homogeneous way, and a fan added to prevent the increasing of the temperature ($T < 30°C$).

A Milestone microwave laboratory system ETHOS TC (Sorisde, Italy) equipped with 10-vessel position carousel was used; the instrument is controlled for temperature.

Visiprep™-DL solid-phase extraction vacuum manifolds, equipped with integral flow control valves and disposable Teflon® flow control valve liners, were from SUPELCO (Bellefonte, PA). The SPE tubes were 6 mL prefritted polypropylene tubes, and the frits were 6 mL polyethylene frits (20 μm porosity).

MiniMIPs

Synthesis of miniMIPs: Screening for selection of the polymerization conditions.

The experimental procedure was carried out according to the one described by Sellergren and Andersson[18] to prepare miniMIPs. A stock solution was prepared for the scaled down version of the polymerization (Table II). It was obtained by mixing template, crosslinker, initiator, and solvent. The same volume of solvent (7 mL) was used throughout, previously purged with N_2 for at least 5 min.

From each stock solution 118 μL was dispensed into a 1.5-mL glass vial and mixed with 50 μmol of the functional monomer, so that the resulting polymerization mixture of the scaled down version had the following molar composition: 1 : 4 : 20 (template: functional monomer: crosslinker) for EDMA and DVB80, and 1 : 4: 13 for TRIM. The vials ($n = 4$ for each assay) were sealed with a rubber septum and

TABLE II
Preparation of miniMIPs

Polymer	MIP mother solution[a]			Monomer	Polymerization conditions
	Crosslinker	Initiator	Porogen		
MIP-1	EDMA, 25 mmol	AIBN, 0.35 mmol	CH_2Cl_2, 7 mL	MAA, 50 μmol (4 μL)	$T = 60°C$ (water bath) 24 h
MIP-2				4-vinylpyridine, 50 μmol (5 μL)	
MIP-3	EDMA, 25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol (4 μL)	$T = 60°C$ (water bath) 24 h
MIP-4				4-vinylpyridine, 50 μmol (5 μL)	
MIP-5				Acrylamide[b], 50 μmol (15 μL)	
MIP-6	EDMA, 25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol (4 μL)	UV (350 nm) (grande W, 24 h)
MIP-7				4-vinylpyridine, 50 μmol (5 μL)	
MIP-8	EDMA, 25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 9 h)
MIP-9	EDMA, 25 mmol	Phenone, 0.35 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 9 h)
MIP-10	EDMA, 25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 19 h)
MIP-11	EDMA, 25 mmol	phenone, 0.51 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 19 h)
MIP-12	DVB80, 25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 30 h)
MIP-13	TRIM, 16.25 mmol	AIBN, 0.35 mmol	THF, 7 mL	MAA, 50 μmol	UV (350 nm) (2 × 15 W, 24 h)

[a] 1.25 mmol of Irganox 1076 was added as template to all the mother solutions. 118 μL of the mother solution were mixed with the monomer in a 1.5 mL glass vial.
[b] Acrylamide was dissolved in the minimum possible volume of THF and was not soluble in CH_2Cl_2.

purged with nitrogen while being cooled in an ice water bath. Polymerization was induced by heat in a water bath (60°C) or by UV irradiation (350 nm, <30°C).

As a control, nonimprinted polymers (NIP) were prepared for each assay ($n = 4$) and treated in exactly the same way except that the template was omitted from the polymerization stage.

Extraction and rebinding experiments

A volume of 1 mL of the porogen was pipetted into each of the vials containing the blank test and imprinted polymers. The vials were then sonicated for 1 h without heating and the concentration of the released template was quantified in each extract by HPLC-UV. The supernatant was filtered (0.2 μm), diluted, and injected.

The polymers were submitted to several washing steps using ultrasonic agitation until that no bleeding that could potentially interfere in the next rebinding assay was observed. Solvents as methanol or the mixture tetrahydrofuran: acetic acid 9 : 1, with higher polarity than the porogen were used. The concentration of the released template was quantified in most washing fractions by HPLC-UV.

A rebinding experiment was then performed by addition of 1 mL of a solution of the template (1/10 of the concentration of the template in the polymerization mixture) followed by sonication of the vials for 1 h. The polymers were allowed to stand for 24 h, and the concentration of free (unbound) template was determined by HPLC-UV. The rebinding percentage was calculated in the blank and in the imprinted polymers by subtracting the concentration of the template in the supernatant from the initial concentration.

MISPE with MIP synthesized by bulk polymerization

Bulk polymerization

The experimental procedure was carried out according to Sellergren and Andersson[18] considering the polymerization mixture obtained by miniMIPs. To 3.8 mL (20 mmol) EDMA, 0.34 mL (4 mmol) MAA, and 1 mmol Irganox 1076 (or no template for NIP synthesis) in 5.6 mL THF, 40 mg (0.24 mmol) AIBN was added as initiator. The mixture was transferred to thick-walled glass jars. These were sparged with nitrogen for 5 min. Porogen was also previously sparged with nitrogen. The polymerization was photochemically initiated; the jars were symmetrically placed at approximately 10-cm distance from a UV light source. After 22 h, the jars were crushed and the polymers ground in a ball mill with repeated sieving under water to a grain size fraction of 25–40 μm. Fines were removed by repeated sedimentation from acetone.

MIP and NIP were washed using microwave energy to remove the template and other unreacted compounds. Sample weight: approximately 0.5 g, extraction solvent: 50 mL of THF: acetic acid (9 : 1), heating time: 2 min, extraction time: 15 min, temperature: 40°C. The liquid phase was filtered (through ashless filters and 0.2 μm filter) and analyzed by HPLC-UV.

MISPE column

A 250–400 mg amount of the MIP or NIP, respectively, was packed into SPE glass syringe barrels. Prior to the use, the columns were conditioned with 3 mL of THF : hexan (3 : 1; v/v). 2 mL of sample were loaded onto the column. The olive oil sample consisted of 0.75 g of olive oil fortified with Irganox 1076 to 30 mg L^{-1} and diluted until 2 mL with THF : hexane in the ratio of 3 : 1. The retained Irganox 1076 was eluted using 3 mL of THF:acetic acid (9 : 1). The obtained extract was evaporated until a final volume of 2 mL under N_2 stream and analyzed by HPLC-UV.

MISPE with MIP synthesized by precipitation polymerization

Precipitation polymerization

The mixtures were prepared and treated in the same way than those for bulk polymerization except that a larger volume of solvent, 40 mL of THF, was employed. After 24 h of polymerization under UV, a gel was obtained from every mixture. It was dried at 40°C around 2 h obtaining a fine powder.

MISPE column

A similar protocol as that described earlier was followed, at vacuum. Previously to the assay MIP and NIP were washed in the own column instead of using microwave energy. Amount of MIP or NIP in each column ($n = 2$): 200 mg; washing: repeatedly with THF : acetic acid (9 : 1) until no Irganox 1076 was detected; conditioning: 6 mL of THF; sample: 0.75 g of olive oil fortified with Irganox 1076 to 15 mg L^{-1} and diluted until 2 mL with THF; elution: 6 mL of THF : acetic acid (9 : 1). The obtained extracts were evaporated until a final volume of 2 mL under vacuum and analyzed by HPLC-UV.

HPLC analysis

HPLC-UV analyses were performed in a Waters Alliance 2695 system equipped with a quaternary pump, autosampler with the volume injection set to

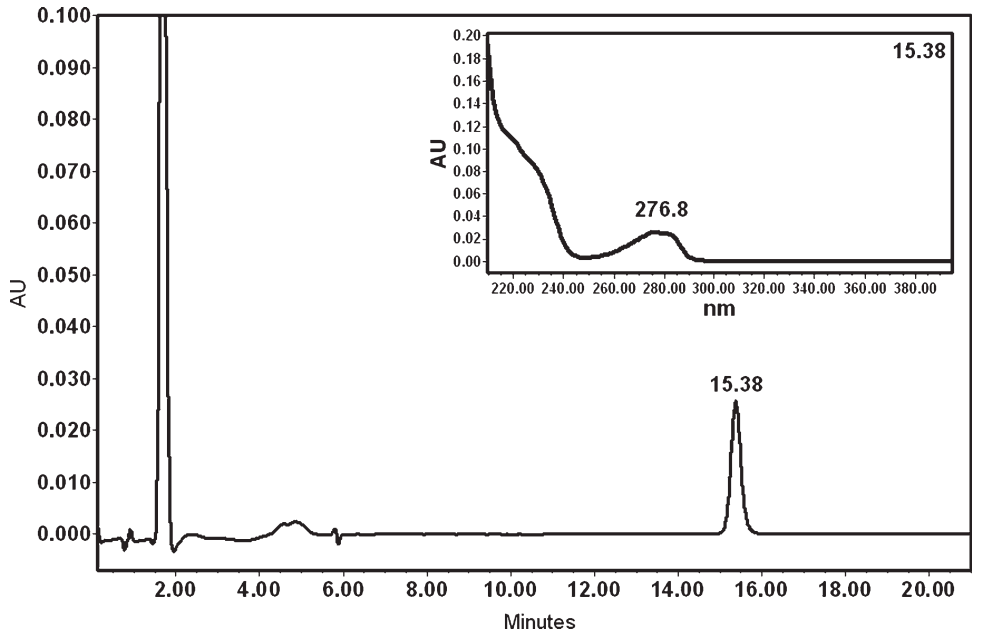


Figure 1 HPLC-UV chromatogram and absorption spectrum of Irganox 1076 (50 mg L^{-1}).

20 μL, and a Waters 996 photodiode array detector. Chromatographic separation was performed on a reversed-phase SunFire C_{18} analytical column (3.0 mm × 150 mm, 3.5 μm particle diameter) from Waters, hold at 30°C. The gradient mobile phase consisted of methanol and water and it was programmed as follows: from 70% of methanol to 100% in 2 min, with a hold of 20 min. Flow rate was 0.5 mL min^{-1}. The signal acquired from the detector was recorded by a personal computer operating under the Empore Pro software v. 5.0 (Waters).

Irganox 1076 was identified by comparison of its retention time with the corresponding peak in the standard solution and its UV spectrum (Fig. 1). It was quantified at 276 nm using a calibration plot of an external standard.

Spectroscopic analysis

Spectrophotometric analysis was performed on Cary 100 Conc UV–vis Spectrophotometer (Varian, USA).

The changes in absorption spectra of Irganox 1076 were recorded by adding MAA into a constant concentration of Irganox 1076 solution (50 mg L^{-1}) in THF. Corresponding MAA solutions omitting Irganox 1076 were used as blank.

RESULTS AND DISCUSSION

Initial tests: Solubility and stability

Some initial tests have been performed using the standard protocol[18] to test whether this compound was suited for imprinting or not. Irganox 1076 solubility and stability were checked: the analyte showed to be soluble in dicloromethane and tetrahydrofuran at the high concentrations levels necessary for imprinting. The stability of the solution of Irganox 1076 (approximately 10,000 mg L^{-1}) was also confirmed in these solvents under the polymerization conditions, at 60°C (water bath), or UV irradiation (temperature lower than 30°C) during 24 h. At comparing with the corresponding standard solutions kept at 4°C, recoveries between 86 and 110% were obtained.

Synthesis of miniMIPs

The influence of five variables on the performance of the MIP was tested, namely porogen, initiation method, monomer, initiator, and crosslinker. The experimental conditions to prepare the polymers are shown in Table II. Degasification with N_2 showed to be an important parameter to control through the experimental study because of the simultaneous presence of the phenolic compound and oxygen that could inhibit the polymerization.[20]

The polymers that showed complete or approximately complete release using the corresponding porogen as solvent were discarded, whereas those that showed to retain the template were subjected to the wash and rebinding steps. Considering that the lack of grinding can make the process slower,[19] rebinding time was 22–24 h to allow to get the desorption equilibrium.

A first screening to select the porogen, functional monomer and initiation method was carried out according to Figure 2.

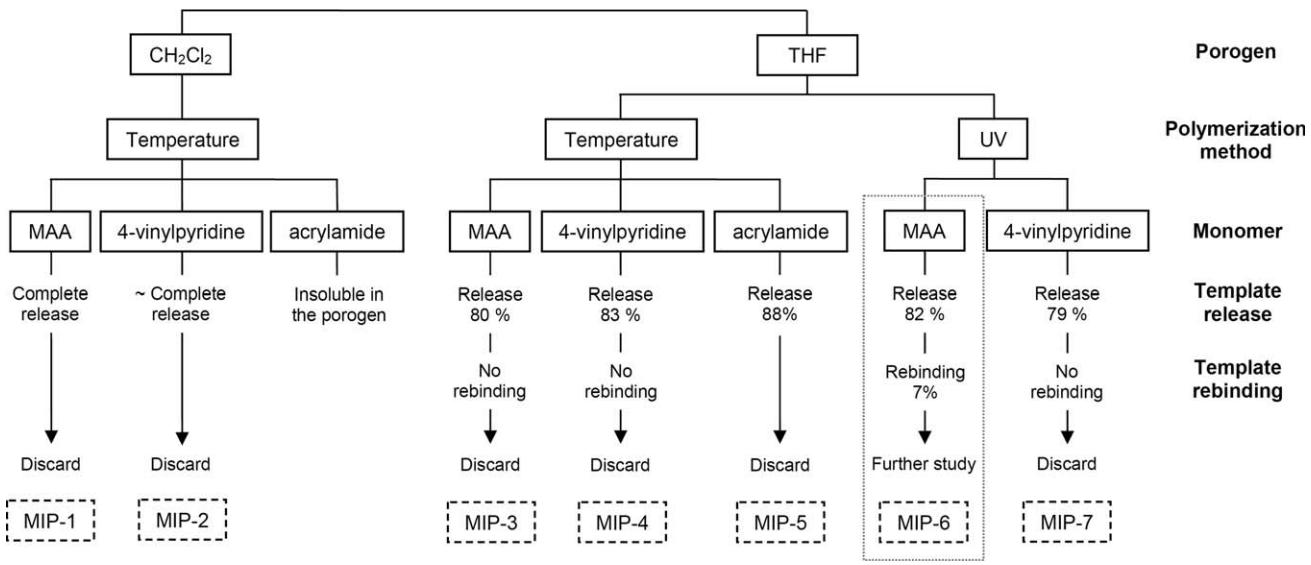


Figure 2 Selection of the monomer, porogen, and polymerization method. Experimental conditions according to Table I.

Porogen

Analyte binding properties of molecularly imprinted sorbents are influenced by the type of solvent, or porogen, used in the polymer synthesis and the solvent used in the particular application of the MIP.[21] As porogen, it is a general procedure to choose an aprotic solvent, as apolar as possible without compromising the solubility of the template.[8] So, THF and dichloromethane were initially selected considering their low polarity and the good solubility shown by Irganox 1076 in these solvents, as reported earlier.

All the polymers synthesized in dichloromethane with either MAA (MIP-1) or 4-vinylpyridine (MIP-2) were discarded because of the almost complete release of the template observed (Fig. 2). The best results obtained with THF were ascribed to its lower polarity.

Initiation method

According to the references, temperature can have a double effect on the imprinted polymer: low temperature is an advantage to stabilize the monomer-template assemblies but a higher temperature polymerization is favorable for the complete polymerization reaction and therefore to improve the number and quality of MIP recognition sites.[22] The comparison between these methods, photo- or thermal polymerization, has showed different results: while He et al.[22] did not find important differences, other authors[21,23,24] recommended the use of photo-ionization at low temperature to improve the properties of the obtained polymers.

In the first assays thermal polymerization at 60°C or photo-initiation at room temperature was used, both during 24 h. Results were analyzed considering MIP-3 and MIP-4 for thermal polymerization and MIP-6 and MIP-7 (Fig. 2) for photo-initiation: similar release (around 80%) was obtained. Considering also the references reported earlier, photo-initiation was selected as polymerization method. To prevent the increasing of the room temperature around the vials, a reactor with two smaller UV lamps and a fan was built in the own laboratory. It was used for the next assays allowing a temperature lower than 30°C.

Functional monomer

Functional monomer is considered to be the most important variable to select for imprinting.[9] Once Irganox 1076 could potentially present either acidic or basic behavior due to its structure with one phenolic group and one carboxylate (Table I), three monomers were compared: MAA, 4-vinylpyridine, and acrylamide (Table I). They are classified as acidic, basic, and uncharged, respectively.[18] All these monomers have been previously reported for imprinting of phenolic compounds: acrylamide for catechin[25] or quercetin[26,27]; 4-vinylpyridine for phenol[28] and quercetin[4]; MAA for quercetin[29] or flavonol.[30]

Acrylamide was discharged (MIP-5) because of its worse compatibility with the porogens used and it did not show any advantage for the imprinting of the template compared to the other monomers. The polymers synthesized with MAA (MIP-3, 6) or 4-vinylpyridin (MIP-4, 7) in THF were subjected to the rebinding step (Fig. 2). The best rebinding results (7.5%) were achieved using MAA as monomer, THF as porogen, and UV radiation as polymerization method (MIP-6). Irganox 1076 was loaded in THF :

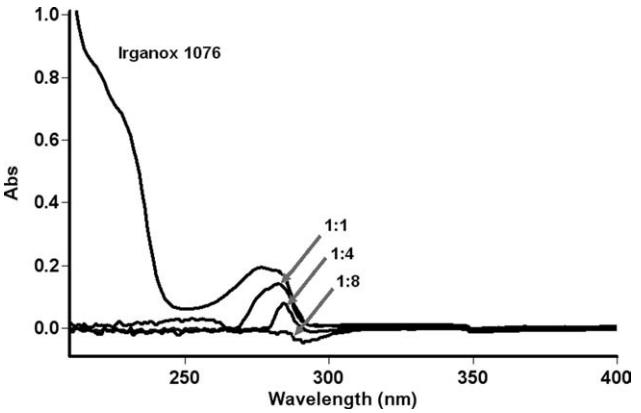


Figure 3 UV absorption spectra of Irganox 1076 in the presence of various concentrations of MAA. [Irganox 1076] = 50 mg L^{-1}, molar ratio Irganox 1076 : MAA 1 : 1, 1 : 4, 1 : 8. Corresponding MAA solution without Irganox 1076 as blanks.

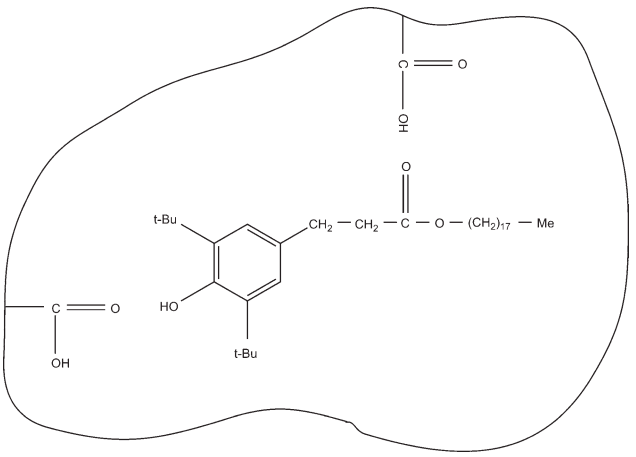


Figure 4 Schematic illustration of the possible interaction between Irganox 1076 and methacrylic acid.

hexan (3 : 1), with the addition of hexan to decrease the polarity of the solvent.[30]

Therefore, methacrylic acid was chosen as monomer. The acidic MAA showed to be more suitable to bind to Irganox 1076 than the other tested monomers, the basic 4-vinylpyridine, or the uncharged acrylamide.

Interaction between MAA and Irganox 1076 in THF was confirmed carrying out a spectroscopic analysis to study the interaction between the monomer and the template, as proposed by He et al.[22] The UV spectral changes upon the addition of MAA to Irganox 1076 solution with ratios template: functional monomer of 1 : 1, 1 : 4, and 1 : 8 are shown in Figure 3. The UV absorption band characteristic of Irganox 1076 is obviously decreasing with increasing the concentration of MAA. This result allows us to think that a stable functional monomer: template interaction is formed in the prepolymerization solution, and the ratio 1 : 4 was kept for the next assays.

A schematic illustration of the possible interaction between monomer and template is shown in Figure 4.

Selection of the initiator

The influence of the type of initiator in the polymer performance has been shown by Mijangos et al.,[24] that compared the use of azo and phenone derivatives recommending the synthesis of the MIP for a long period of time using low concentration of initiator and low temperature.

In the study herein, a set of polymers were imprinted using also two types of initiators (Table II): AIBN (azo), commonly used for thermal and photo-initiation[18,24] or 2,2 dimethoxy-2-phenylacetophenone (phenone), a photo-initiator.[24,31]

A first set of experiments was carried out using the same molar amount of both initiators with a polymerization time of 9 h (MIP-8, MIP-9). The progress of the polymerization seemed to be quicker with AIBN than with the phenone, although 9 h showed to be an insufficient time for both.

In the next assay, the phenone proportion was increased until 1% respect to the total mass (g) of the mixture and the polymerization time until 19 h, which showed to be suitable for completeness polymerization (MIP-10 and MIP-11). The best rebinding results were obtained using AIBN (Fig. 5), whereas that for phenone lower selectivity was achieved, with similar result for MIP and NIP, that may be due to the higher percentage of initiator used.[24]

Selection of the crosslinker

The crosslinker "freezes" the template-monomer complex upon polymerization and provides the polymeric backbone leading to the polymer mechanical stability.[9] The effect of three crosslinkers selected considering their different structures (Table I) was compared:

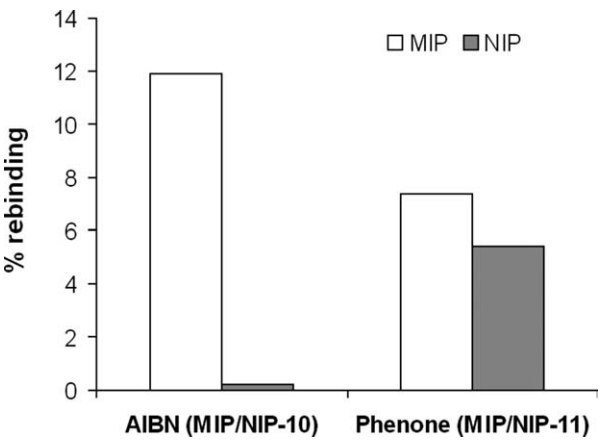


Figure 5 Selection of the initiator. Experimental conditions according to Table I.

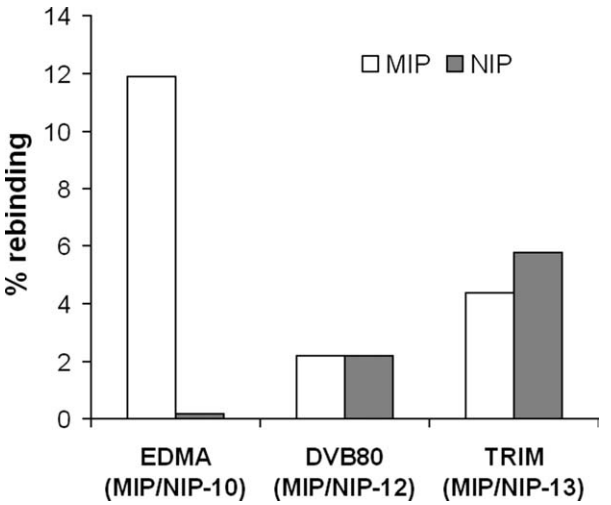


Figure 6 Selection of the crosslinker. Experimental conditions according to Table I.

ethylene glycol dimethacrylate, EDMA; trimethylolpropane trimethacrylate, TRIM; and divinylbenzene, DVB 80 (MIP-10, MIP-12, and MIP-13).

Both methacrylates EDMA and TRIM have two and three similar functional groups, respectively, being EDMA more rigid and TRIM more flexible. EDMA has been commonly used for imprinting[18] while TRIM has been suggested in the last years to imprint large molecules because of the possibly improved mass transfer in low crosslinking density polymers.[32] On the other hand, DVB80 lacks oxygen groups and can only establish π-π interaction with the template and it is known to enhance the rigidity of the polymer chains.[33]

Depending on the crosslinker used, different template:monomer:crosslinker ratios were used (Table II): for EDMA and DVB80, the most common 1 : 4 : 20, as suggested in the Sellergren and Andersson protocol.[18] For TRIM, the ratio was decreased until 1 : 4 : 13 considering previous studies.[32] Polymers synthesized with DVB80 or TRIM needed a longer polimerization time than EDMA.

The best results for each assay were obtained loading the sample in THF for TRIM or in THF: hexan 3 : 1 for EDMA and DVB80. EDMA allowed obtaining both the highest recovery values for MIP and the highest specificity compared to the NIP (Fig. 6).

Application of the MISPE for cleanup of olive oil spiked with Irganox 1076

The possible application of the imprinted polymer as a cleanup method of a complex matrix was tested using olive oil fortified with Irganox 1076 as sample. Two types of MIPs prepared by bulk and precipitation polymerization were tested, packing 400 or 200 mg of polymer in each column respectively.

In the rebinding assay, the percentage of Irganox 1076 retained from the sample of olive oil raised from 17 to 42% for the MIP prepared using bulk polymerization and precipitation polymerization, respectively. For this last MIP prepared using precipitation polymerization, 92% of the retained Irganox 1076 could be eluted allowing the cleaning up of the matrix.

CONCLUSIONS

This work has presented an initial approach to prepare a MIP of Irganox 1076, a previously nonimprinted target. The influence of five variables namely monomer, crosslinker, porogen, polymerization, and initiator was explored achieving the most promising results with MAA, EDMA, and AIBN in THF under UV radiation. The application of MISPE to determine Irganox 1076 in olive oil showed the potential of the imprinted polymer as clean up method of complex matrices.

References

1. Masquè, N.; Marcè, R. M.; Borrull, F. TrAC Trends Anal Chem 2001, 20, 477.
2. Muldoon, M. T.; Stanker, L. H. Anal Chem 1997, 69, 803.
3. He, C.; Long, Y.; Pan, J.; Li, K.; Liu, F. J Biochem Biophys Methods 2007, 70, 133.
4. Molinelli, A.; Weiss, R.; Mizaikoff, B. J Agric Food Chem 2002, 50, 1804.
5. Puoci, F.; Garreffa, C.; Iemma, F.; Muzzalupo, R.; Spizzirri, U. G.; Picci, N. Food Chem 2005, 93, 349.
6. Schirmer, C.; Meisel, H. J Chromatogr A 2006, 1132, 325.
7. Baggiani, C.; Anfossi, L.; Giovannoli, C. Anal Chim Acta 2007, 591, 29.
8. Andersson, L. I. J Chromatogr B 2000, 739, 163.
9. Bergmann, N. M.; Peppas, N. A. Prog Polym Sci 2008, 33, 271.
10. Commission Directive 2002/72/EEC. Office J Eur Communities 2002, L220, 18; Corrigendum OJ L39 13/2/2003, p 1.
11. Council Directive 85/572/EEC. Off J Eur Communties 1985, L372, 14.
12. Dopico-García, M. S.; López-Vilariño, J. M.; González-Rodríguez, M. V. J Chromatogr A 2003, 1018, 53.
13. Dopico-García, M. S.; López-Vilariño, J. M.; González-Rodríguez, M. V. Talanta 2005, 66, 1103.
14. Farajzadeh, M. A.; Bahram, M.; Jönsson, J. A. Anal Chim Acta 2007, 591, 69.
15. O'Brien, A. P.; Cooper, I.; Tice, P. A. Food Addit Contam 1997, 14, 705.
16. Helmroth, I. E.; Dekker, M.; Hankemeier, T. Food Addit Contam 2002, 19, 176.
17. Dopico-Garcia, M. S. Ph.D. Thesis. University of Coruña; 2005.
18. Sellergren, B.; Andersson, L. I. Methods 2000, 22, 92.
19. Takeuchi, T.; Fukuma, D.; Matsui, J. Anal Chem 2000, 71, 285.
20. Caldwell, R. G.; Ihrig, J. L. J Am Chem Soc 1962, 84, 2878.
21. O'Shannessey, D. J.; Ekberg, B.; Andersson, L. I.; Mosbach, K. J Chromatogr 1989, 470, 391.
22. He, J.; Zhu, Q.; Deng, Q. Spectrochim Acta Part A 2007, 67, 1297.

23. Lanza, F.; Hall, A. J.; Sellergren, B.; Bereczki, A.; Horvai, G.; Bayoudh, S.; Cormack, P. A. G.; Sherrington, D. C. Anal Chim Acta 2001, 435, 91.
24. Mijangos, I.; Navarro-Villoslada, F.; Guerreiro, A.; Piletska, E.; Chianella, I.; Karim, K.; Turner, A.; Piletsky, S. Biosens Bioelectron 2006, 22, 381.
25. Blahová, E.; Lehotay, J.; Skacáni, I. S. J Liq Chromatogr Relat Technol 2005, 27, 2715.
26. Xie, J.; Chen, L.; Li, C.; Xu, X. J Chromatogr B 2003, 788, 233.
27. Xie, J.; Zhu, L.; Luo, H.; Zhou, L.; Li, C.; Xu, X. J Chromatogr A 2001, 934, 1.
28. Lv, Y.-Q.; Lin, Z.; Feng, W.; Tan, T. Chromatographia 2007, 66, 339.
29. Xia, Y.; Guo, T.; Song, M.; Zhang, B.; Zhang, B. React Funct Polym 2006, 66, 1734.
30. Suárez-Rodríguez, J. L.; Díaz-García, M. E. Anal Chim Acta 2000, 405, 67.
31. Xia, W. Z.; Cook, W. D. Polymer 2003, 44, 79.
32. Yu, C.; Mosbach, K. J Chromatogr A 2000, 888, 63.
33. Michailof, C.; Manesiotis, P.; Panayiotou, C. J Chromatogr A 2008, 1182, 25.
34. Ellwanger, A.; Berggren, C.; Bayoudh, S.; Crecenzi, C.; Karlsson, L.; Owens, P. K.; Ensing, K.; Cormack, P.; Sherrington, D.; Sellergren, B. Analyst 2001, 126, 784.